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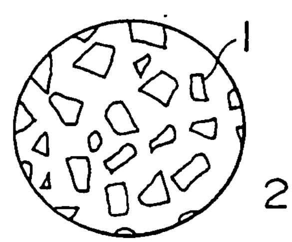
(54) Functional ceramic shaped article and process for producing the same.

(57) Functional ceramic shaped articles resistant to oxidation and corrosion can be produced with high dimensional accuracy by mixing (i) particles (1) and/or fibers of at least one functional inorganic material selected from piezoelectric materials such as $PbTiO_3$ and $PbZrO_3$, dielectric materials such as TiO_2 and $MgTiO_3$, magnetic materials such as Fe, Co, and Ni, heat conductive materials such as diamond and CBN, catalytically active materials such as γ-Al_2O_3 and zeolites, electron emissive materials such as W and Th-W, sensor materials such as NiO and FeO, and biological materials such as Al_2O_3 and apatite with (ii) particles of at least one of metals of groups III, IV, V, VI, and VIII of the periodic table, followed by shaping and reaction-sintering those mixtures.

FIG. 1



EP 0 331 160 A2

FUNCTIONAL CERAMIC SHAPED ARTICLE AND PROCESS FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to functional ceramic shaped articles and a process for producing the same. More particularly, the invention relates to functional ceramic shaped articles which are producible by sintering shaped bodies with a small dimensional change in sintering stage and have each at least one function selected from piezoelectric, dielectric, magnetic, heat conducting, electron emitting, catalytic, sensing and biological functions, the resistivity of said articles being variable from an insulator level to a conductor level with the kinds and proportions of ingredients used, and said articles being superior in oxidation resistance and corrosion resistance, and the invention also relates to a process for producing such functional ceramic shaped articles.

DESCRIPTION OF THE RELATED ART

Recently, research and development for functional ceramic materials has been made extensively and in particular, ceramic materials having gradient functions have drawn attention. However, no satisfactory functional ceramic material has been developed up to now. There are needs today for functional ceramic materials which satisfy all of various requirements about functions, shapes simple or complicated which are fitted for a number of applications, dimensions and accuracy thereof, etc. Especially, it is contemplated to develop a shaped ceramic material not having a single function but a plurality of functions and if necessary, one or more functionally gradient functions.

Japanese Patent Kokai (Laid-Open) No. 62-292666 proposes a process for producing functional ceramics which comprises normal-pressure sintering of raw material mixtures containing a sintering aid. Japanese Patent Koaki (Laid-Open) No. 61-242978 proposes a process for producing functional ceramics which comprises impregnating Si_3N_4 sintered bodies, which are porous products of reaction-sintering, with a biological material (material useful in living bodies) such as apatite.

On the other hand, the following several processes are proposed which, though not for producing functional ceramics, use reaction-sintering techniques to produce machine-constructing materials. That is, processes described in Japanese Patent Kokai (Laid-Open) Nos. 61-101465, 61-201662, 61-256906, 62-223065, and 62-270481. However, none of these patent applications disclose any reaction-sintered article having an electric or magnetic characteristic, in other words, a special function.

In general, functional materials, for example, well-known magnetic materials according to the prior art include representative magnets of Fe and Ni families, Fe-Cr-Co magnets, ferrite magnets and sintered rare earth metal-Co magnets. These magnetic materials, however, have disadvantages such as high costs, brittleness and hence liability to break, difficulties in making large-size articles, and low resistance to oxidation, corrosion, or heat. Hence, these materials are unifitted for uses in special or harsh environments.

There are bond magnets, which are developed for offsetting the above disadvantages. These magnets are formed by binding magnetic particles with plastics or synthetic rubbers. This covers the drawback of being hard and brittle, but the maximum service temperature of these magnets is 120°C or below, that is, they are inferior in heat resistance corrosion resistance, and oxidation resistance.

According to processes comprising sintering functional ceramic powders to give shaped articles, the resistance to heat, corrosion, and oxidation, if obtained, will not be provided with complicated shapes by conventional normal-pressure sintering or HIP sintering and multi-functional shaped articles are difficult to obtain. It is more difficult in this case to obtain shaped articles having gradient functions.

SUMMARY OF THE INVENTION

An object of the present invention is to provide functional ceramic shaped articles which are superior in heat resistance, corrosion resistance, and oxidation resistance, producible by sintering with high dimensional accuracy and precision, and are provided each with at least one property or function selected from a piezoelectric function, dielectric property, magnetic property, thermal conductivity, electron emissivity,

catalytic activity, sensing function, and biological functions, the resistivity of said shaped articles being variable from an insulator level to a conductor level.

Another object of the present invention is to provide a process for producing such functional ceramic shaped articles.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic cross-sectional view of an example of the functional ceramic shaped article consisting of a sintered body produced according to this invention.

Fig. 2 is a schematic cross-sectional view of an article made by covering the surface of the article of Fig. 1 with a film superior in oxidation resistance and corrosion resistance.

Figs. 3 - 6 are schematic cross-sectional views of functional ceramic shaped articles prepared by reaction-sintering in Example 5 which is given later.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention involves (i) a functional ceramic shaped article consisting of a reaction-sintered body which has high dimensional accuracy and a specific electrical, magnetic, or thermal property, said reaction-sintered body being formed of particles and/or fibers of at least one functional inorganic material selected from the group consisting of piezoelectric materials, ferroelectric materials, low-dielectric materials, magnetic materials, highly heat conductive materials, low heat conductive materials, catalytically active materials, electron emissive materials, sensor materials, and biological materials, said particles and/or fibers being bound together through a ceramic formed from a metal powder during the sintering and (ii) a process for producing such articles.

This article is a novel material that could not be obtained at all by normal-pressure sintering or HIP sintering. The present inventors have found that a functional ceramic shaped article superior in oxidation resistance and corrosion resistance can be obtained by embedding functional inorganic particles such as piezoelectric particles in a matrix consisting of metal particles, and reaction-sintering this matrix to convert it to a ceramic which binds together said inorganic particles, thus forming a strong sintered body, and that ceramic articles of complicated shapes can also be produced with high dimensional accuracy according to this process. For instance, electro-conductivity can be added to a catalytic activity. Furthermore, when catalytically active particles are combined with other functional particles such as magnetic particles, heat conductive particles, or electron emissive particles, it is possible to produce dielectric shaped articles having other additional functions. Thus, the applications of the present articles can be expanded to a great extent.

According to this invention, functional particles are bound together through an inorganic compound formed from metal particles during the sintering and thereby voids among particles are reduced. Hence the dimensional change in sintering stage can be reduced. Further, the resistivity of sintered articles can be controlled to an optional value ranging from an insulator level to a conductor level by suitable choice of raw material inorganic compounds. This can also be achieved by binding together particles and/or fibers (short filaments) of at least one functional inorganic compound through a nitride formed from metal particles.

Reaction products resulting from the reaction sintering according to this invention contain whiskers and/or similar particles, through which other particles can be bound strongly.

Metal particles used in this invention consist of at least one of groups III, IV, V, VI, and VIII metals of the periodic table, particularly at least one of Ti, Zr, V, Nb, Ta, Cr, Ce, Co, Mn, Hf, W, Mo, Al, Si, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Lu, and Th. The resistivity of these metal particles varies depending upon the kind of metal used and the kind of product formed therefrom during the reaction-sintering. Accordingly, the resistivity can be controlled to an optional value in the range of an insulator level to a conductor level by combining together different metals cited above or different reaction products formed therefrom. For example, the resistivity of Ti nitride is as low as about 10^{-5} Ωcm and the resistivity of Si nitride, on the contrary, is as high as about 10^{15} Ωcm. As to the magnetic properties, the loss caused by eddy currents in alternating magnetic fields can be reduced by increasing the resistivity.

In this invention, existing dielectric materials may be used including TiO_2, $MgTiO_3$, $CaTiO_3$, $SrTiO_3$, La_2O_3-$2TiO_2$, SiO_2, ZnO-TiO_3, Bi_2O_3-$2TiO_2$, $BaTiO_3$, and Pb(Zr, Ti)O_3. These dielectric materials when used provide low-dielectric or high-dielectric articles which exhibit high breakdown voltages.

The use of dielectric materials with less relative dielectric constants than 500 provides lower-dielectric

articles while the use of dielectric materials with more relative dielectric constants than 500 provides higher-dielectric articles. Small-size, high-capacity, single-body laminated capacitors can be produced by sintering high-dielectric layers superposed one upon another. According to this invention, phases different in resistivity can be formed by binding together dielectric particles through a metal nitride, phase- boundary polarization can be readily achieved. Binding with an electrically conductive nitride provides highly conductive, dielectric articles.

Piezoelectric constants of the usable piezoelectric materials cover a wide variety of values, for example, from 2 x 10^{-12} m/V (C/N) of quartz to 300 x 10^{-12} m/V (C/N) of PZT. Applications of the piezoelectric articles include piezoelectric gas lighters (for firing gases) that generate voltages on exerting force, filters in radio and television receivers, and piezoelectric buzzers and ultrasonic oscillators that vibrate on applying voltage. According to this invention, piezoelectric ceramic articles superior in heat resistance can be obtained with ease by binding together piezoelectric particles through a metal nitride. The binding through a conductive nitride provides conductive, piezoelectric articles.

In this invention, existing piezoelectric materials may be used including $PbTiO_3$, $PbZrO_3$, $BaTiO_3$, Pb-(Zr, Ti)O_3, and (Pb, Sr) (Zr, Ti)O_3.

The magnetic material for use in this invention consists of at least one of Fe, Co, Ni, Gd, and Dy metals and Fe, Co, Ni, Gd, Dy, Mn, Cr, Eu, and Cu compounds, particularly at least one of Fe, Co, Ni, Gd, Dy, Cu_2MnAl, Cu_2MnIn, MnB, Fe_3C, Mn_4N, MnBi, MnSb, MnAs, CrFe, CrO_2, EuS, EuO, CoPt, Fe_3Al, $MnFe_2O_4$, $FeFe_2O_4$, $SmFeO_3$, $CoFe_2O_4$, $NiFe_2O_4$, MnBi, $CuFe_2O_4$, $Li_{0.5}Fe_{2.5}O_4$, $MgFe_2O_4$, $Y_3Fe_5O_{12}$, $Gd_3Fe_5O_{12}$, Fe_3O_4, Fe_2O_3, $BaFe_{12}O_{19}$, and $La_{0.5}Ca_{0.5}MnO_3$. Magnetic properties such as the magnetic flux density and magnetic permeability of products can be controlled as desired by mixing two or more of these magnetic materials in suitable proportions.

Usable electron emissive materials include thermoelectron emissive materials, field electron emissive materials, secondary electron emissive materials, photoelectron emissive materials, and exoelectron emissive materials. According to this invention, the current density is sintered products is free to choose since the resistivity thereof can be varied optionally. In addition, currents through sintered products can be kept constant because of the superior oxidation resistance thereof, in other words, because of the high heat stability of the surface composition thereof.

In this invention, existing electron emissive materials can be used including W, Th-W, LaB_6, (Ba, Sr, Ca)O, Zr-W, TiC, TaC, MgO, $SbCs_3$, BeO, $CaSO_4$, and Ag-O-Cs.

Heat conductive materials for use in this invention are desired to have thermal conductivities of at least 0.1 cal/cm•sec•°C (ambient temperature). According to this invention, the resistivity can be varied optionally by binding together with different ceramics.

In this invention, existing highly heat conductive materials may be used including diamond, CBN, and Be-doped SiC.

Catalytically active materials for use in this invention may also be existing materials in use for petroleum refinary catalysts, vapor-phase oxidation catalysts, automobile exhaust gas treatment catalysts, denitration catalysts, etc. According to this invention, porous sintered articles can be readily obtained by binding together inorganic particles through a ceramic formed from metal particles. Since the resistivity also can be controlled, self-heating catalysts can be produced.

Specific examples of the existing catalyst materials for use in this invention include γ-Al_2O_3, zeolite, SiO_2, steatite, cordierite, zirconia, and mullite.

In this invention, existing biological materials may be used including Al_2O_3, $Ca_3(PO_4)_3$, apatite, and ZrO_2, which are used generally artificial bones, tooth crowns, and tooth roots.

In this invention, existing sensor materials may be used including NiO, FeO, CoO, ZnS, PZT, TaN, AgX (Ag halide), CdS, SiO_2, Al_2O_3, TiO_2, Y_2O_2S, ZrO_2, LiCl, TiO_2-V_2O_5, and SnO_2.

Sensors for detecting or indicating humidities, temperatures, gases, or positions by choosing suitable materials from Al_2O_3, LiCl, ZrO_2, CdS, ZnS, CoO, TiO_2, SnO_2, PZT, etc, which are conventionally used for sensors.

The various functional materials stated above are used in the form of particles desirably passable through 10-mesh screens. When used in fibrous form, these materials produce the same effects but provide anisotropic products.

According to this invention, it is also possible to produce functional ceramic articles controlled in the coefficient of thermal expansion, mechanical strength, oxidation resistance, porosity, corrosion resistance, or infrared emissivity, besides the above stated functions. The foregoing functions may also be provided in combination two or more.

Moreover, functionally gradient ceramic articles, wherein functions change continously or stepwise or ceramic articles having directional functions can be produced by arranging some of the above-stated

functional materials continously or stepwise or orienting some of them, followed by reaction-sintering these arranged or oriented materials. In this invention, the dimensional change from the shaped bodies to the sintered body is minimized since the reaction-sintering method is employed.

In this invention, the porosity of functional ceramic articles is desired to be up to 40%. This is because articles having porosities exceeding 40% are inferior in various properties. The pores in the green shaped bodies need to be mainly open cells, because passages for gas need to be present in said green shaped bodies, containing metal particles, in order that intended articles may be produced by sintering said green shaped bodies in a nitriding atmosphere, thereby nitriding said metal particles. The nitriding atmosphere comprises a nitrogen-containing gas (e.g. nitrogen gas) and optionally hydrogen, oxygen, carbon monoxide, or argon gas. During the sintering, metals in a particle form may react with each other or metal particles may react with functional inorganic particles, depending on the species of metals or on the species of metal and inorganic compound, without raising any problem. For example, some TiAl, $TiAl_3$, TiSi, or ZrAl may form.

In this invention, the sintering may be carried out in an atmosphere of oxidizing gas, carbonizing gas, or oxidizing-nitriding gas, which is other than nitriding gases, whereby functional inorganic particles can be bound together through an oxide, carbide, or oxide-nitride.

As to magnetic articles, those superior in magnetic directionality can be obtained by heating shaped bodies containing magnetic particles, in a magnetic field. Of course, such ceramic articles can also be obtained by heating again sintered bodies containing magnetic particles, in a magnetic field to convert the magnetic particles into paramagnetic particles, followed by cooling the reheated bodies. In addition, ceramic articles having isotropic magnetism can be produced by omitting such treatments as mentioned above.

In this invention, pores in compound ceramic sintered bodies may contain resins, oils, or particles of other kinds. Such sintered bodies can be used as slide members.

Fig. 1 is a cross-sectional view of an example of functional ceramic articles consisting of reaction-sintered bodies 1, 2 produced according to this invention.

Fig. 2 is a cross-sectional view of a magnetic ceramic article made by covering the surface of the article of Fig. 1 with a film 3, such as an Si_3N_4 or Si film, which is superior in oxidation resistance and corrosion resistance.

In this invention, suitable binders for use to shape green bodies include; organic polymers, e.g. polyvinyl butyral and polyethylene; organic Si polymers, e.g. a silicon imide compound, polyethylene-polysilane compound, and polysilicone; and synthetic waxes. Such a binder is added in suitable amounts, preferably from 8 to 15 parts by weight based on the whole ingredient, thereby giving desirably a packed particle volume fraction of shaped body (percentage of volume occupied by powders based on the whole volume of body) of at least 70%.

The shaping is carried out by such a method selected from those hitherto known, including injection molding, press forming, doctor blade method, rubber press forming, extrusion forming, and metal powder forming, as to meet the shape of product, and property requirements and geometric requirements for the product.

Metals and various functional materials including fibers may be used in the form of roundish particles pulverized by using a mill or the like or in the form of granulated powders.

The process of this invention for producing functional ceramic shaped articles comprises adding a binder consisting of a thermoplastic resin to a mixture of the above-stated metal powder with the above-stated functional inorganic power, heating and kneading the whole mixture, subjecting it to hot pressing to shape an aggregate of particles with a packed particle volume fraction of at least 70%, heating the body to remove the binder, and sintering the body by heating in a nitriding gas atmosphere, thereby binding together inorganic particles through nitride particles and/or whiskers formed from the metal powder.

The above binder consisting of a thermoplastic resin is added desirably in an amount represented by

$$B = [(7S/20{,}000) + 3] \pm 2.5$$

wherein, B denotes the amount (part by weight) of binder added to 100 parts by weight of the raw material mixed powders and S denotes the specific surface area (cm^2/g) of the overall raw material powder, and then the whole mixture is kneaded with heating, and an aggregate of particles with a packed particle volume fraction of at least 20% is shaped from the kneaded mixture by hot press forming. In addition, the composition composed of both the powder mixture and the binder consisting of a thermoplastic resin is desired to have an apparent viscosity of $(3\text{-}90) \times 10^4 N \cdot s/m^2$ at 150 °C.

The mixing ratio of the metal powder to the whole mixture is desired to be at least 45% by volume for the purpose of minimizing the dimensional change in sintering stage and yielding sintered ceramic articles having sufficient strength.

Sintered articles having enough strength, e.g. flexural strength of about 300 MN/m^2 or more, can be

obtained by shaping aggregates of raw material particles with packed particle volume fractions of 60% and more. Raising said packed particle volume fraction is most effective in enhancing the strength.

In this invention, the binder consisting of a thermoplastic resin plays an important role, that is, a packed volume fraction of 70% or more of the shaped aggregate of raw material particles can be achieved by adding a controlled amount of this binder.

Particle sizes of the metal powder are up to 10 µm, preferably up to 1 µm, and particle sizes of the inorganic powder are up to 100 µm, preferably up to 20 µm. These materials are used preferably in the form of roundish particles prepared by grinding with a mill or the like, though commercially available powders of suitable particle sizes may be used as such.

The inorganic powder may be replaced partly by whiskers. In this case, whiskers are blended desirably in an amount of up to 55% by volume based on the whole ingredient which will remain after sintering. When the amount thereof exceeds this limit, uniform blending of ingredients is impossible in some cases. Whiskers to be added are desired to have an average aspect ratio of up to 200 and an average length of up to 200 µm.

The ingredient mixture containing the above defined amount of binder (comprising a thermoplastic resin) has an apparent viscosity in the range of (3-90) x $10^4 N \cdot S/m^2$ as will be described later. The fluidity of ingredient mixture during its shaping (before sintering) is predictable from the values of apparent viscosity. Since shaped bodies with packed volume fractions of at least 70% can be obtained by controlling the apparent viscosity within the above-defined range, compositions fitted for near net shape can be provided.

Particularly in view of the flow property of ingredient mixture, it is desirable to use an Si powder of up to 1 µm in particle size and add a binder composed of 15-60% by weight of polyethylene, 30-70% by weight of wax, and 5-25% by weight of stearic acid.

The ingredient mixture containing such a binder is thoroughly kneaded and then shaped. According to the intended shape and required properties of end product, a suitable method can be chosen from injection molding, press forming, rubber press forming, extrusion forming, in-mold powder forming, etc. In any of such methods, the kneaded mixture is warmed and shaped above the softening temperature of the binder resin. As an example, the shaping by use of a mechanical press is better carried out at a pressure of about 1000 kgf/cm^2.

The shaped body is then subjected to deoiling (removal of the binder) prior to sintering. The deoiling can be accomplished by heating the shaped body gradually from room temperature up to about 500 °C at a rate of about 2 °C/hr.

Desirably, the sintering is carried out by heating the deoiled body in a nitriding gas atmosphere composed of nitrogen and/or ammonia and if necessary, hydrogen, argon, or helium at a temperature below the melting point of the metal, particularly form 1100 to 1350 °C. The optimum rate of heating to the sintering temperature is 4 °C/hr. In this manner, the sintering can be accomplished with ease. If necessary, a hot press may be used.

The porosity of sintered bodies is desired to be up to 40%. When the porosity exceeds 40%, the strength is undesirably low. Lower porosities than 40% can be achieved by controlling said packed particle volume fraction of shaped bodies to at least 70%.

When Si is used as a metal ingredient, Si_3N_4 whiskers are produced during the sintering. The content of these whiskers is desirably from 1 to 70%, particularly from 10 to 30%, by volume based on the reaction product phase.

The following things are conceivable about the reason why the dimensional change of shaped bodies in sintering stage is minimized (about 0.15% or less) according to this invention.

That is, in the first place, nitride whiskers formed by the sintering in a nitriding atmosphere contribute greatly to the dimensional change in sintering stage. The content of these whiskers is controlled desirably within the range of 1 to 30% by volume based on the formed nitride. This whisker content depends on the amount of metal used and other factors.

When a composition of 100 parts by weight of a metal-inorganic compound mixture and 9 parts by weight of a thermoplastic resin binder is kneaded with heating and shaped by hot press forming and the shaped body is freed of the binder and sintered, the amount of whiskers and the strength of sintered body increase as the amount of metal used is increased. Simultaneously, the dimensional change in sintering stage increases but this increase is not so great as to raise a problem in practical use. This is conceivably because particles in the sintered body are strongly connected one to another through whiskers formed during the sintering.

The raw material powders themselves, consisting of fine brittle solid particles, are difficult to pack densely when compressed as such. Therefrom, it is necessary to aid the flow of these particles by adding the above-stated binder and therewith enhance the strength of shaped body. The strength of sintered body

varies depending on the amount of binder added. As stated above, this strength is related to the packed volume fraction (density) of the shaped body. As the amount of binder is increased, flow properties of the mixture become better and the press forming thereof becomes easier, resulting in an increase in the packed particle volume fraction of the shaped body. When the binder is added in larger amounts than that giving the ideal densely packed state of raw material particles, these particles become in such a state as to be isolated one from another. In this case, the mixture exhibits a high fluidity, but the solid fraction of shaped body lowers excessively, that is, the volume occupied by solid particles in the shaped body reduces greatly, and as a result the sintered body has a high porosity and a low strength.

As stated above, shaped bodies of proper composition in preferred embodiments of this invention are sintered by heating in a nitriding atmosphere, whereby whiskers formed from metal particles grow three-dimensionally, connect solid particles one to another, and simultaneously fill interstices between these particles, hence yielding ceramic articles having high stiffness and toughness.

This invention is illustrated in more detail with reference to the following examples.

The specific surface area S(cm^2/g) of the raw material powder can be calculated from the following formula:

$$S = \frac{6}{\rho \cdot d}$$

wherein ρ is the density (g/cm^3) of powder particles and d is the average diameter (cm) of powder particles.

Example 1

9 Parts by weight each of organic binders: a polyethylene wax, other synthetic wax, and stearic acid, for shaping purposes was added to 100 parts by weight of a mixture composed of 30 wt% of metallic Si powder of 1 μm in average particle size and 70 wt% of a metallic Fe powder (used as a magnetic material) of 20 μm in average particle size. The resulting mixtures were kneaded each in a pressurized kneader at 160° C for 5 hours. These kneaded mixtures were crushed to prepare test materials. Hollow cylinders of 30 mm in inner diameter, 50 mm in outer diameter, and 10 mm in thickness were shaped from the test materials by using a mechanical press at a pressure of 1000 kgf/cm^2 and a temperature of 160° C. These shaped cylinders were found to have packed particle volume fractions (not including binder volume fractions) of at least 60%. The shaped cylinders were heated up to 500° C at a heating rate of 3° C/hr in an argon atmosphere to remove the binder, and further heated stepwise from 500° C to 800° C at a heating rate of 2° C/min and from 800° C to 1500° C from a long time in a nitrogen atmosphere while applying a magnetic field of 3000 gauss, yielding sintered articles. Properties of these sintered articles are shown in Table 1. Therefrom it can be seen that these articles are magnetic ceramics.

These sintered articles were found to contain about 5 vol % of silicon nitride whiskers.

Table 1

Dimensional change in sintering stage (%)	Resistivity (Ωm)	Magnetic flux density (gauss)	Flexural strength (MPa)
0.8	3×10^4	1000	360

Example 2

According to the procedure of Example 1, pieces were shaped from 30 wt% of a Ti powder of 1 μm in average particle size and 70 wt% of a γ-Fe_2O_3 powder of 1 μm in average particle size, and then heated stepwise from 500° C to 1300° C for a long time in a nitriding atmosphere while applying a magnetic field of 3500 gauss, yielding sintered articles. Properties of the obtained sintered articles are shown in Table 2. Therefrom it can be seen that these articles are magnetic ceramics.

The content of titanium nitride whiskers in these sintered articles was similar to that in the articles obtained in Example 1.

Table 2

Dimensional change in sintering stage (%)	Resistivity (Ωm)	Magnetic flux density (gauss)	Flexural strength (MPa)
1.0	5×10^{-6}	1200	340

Example 3

According to the procedure of Example 1, pieces were shaped from 30 wt% of an Al powder of 1 μm in average particle size and 70 wt% of a $PbTiO_3$ powder of 1 μm in average particle size, and then heated stepwise from 400°C to 1100°C for a long time in a nitriding atmosphere, yielding sintered articles. The dielectric constant of the obtained articles was 250. The content of aluminum nitride whiskers in these sintered articles was similar to that in the articles obtained in Example 1.

Example 4

According to the procedure of Example 1, pieces were shaped from 30 wt% of a Ti powder of 1 μm in average particle size and 70 wt% of an Al_2O_3 powder of 1 μm in average particle size, and heated stepwise from 400°C to 1100°C for a long time in a nitriding atmosphere, yielding sintered articles. The dielectric constant of the obtained articles was 9. The content of titanium nitride whiskers in these sintered articles was similar to that in the articles obtained in Example 1.

Example 5

7 parts by weight of a polyethylene family thermoplastic resin was added to 100 parts by weight of a mixture composed of 50 wt% of a metallic Si powder of 0.9 μm in average particle size and 50 wt% of a Co powder of 1 μm in average particle size. The resulting mixture was kneaded in a pressurized kneader at 160°C for 4 hours. The kneaded mixture was crushed to a size of 10 mesh or less to prepare the raw material of insulating magnetic ceramics A. On the other hand, 5 parts by weight of a polyethylene family thermoplastic resin was added to 100 parts by weight of a mixture composed of 80 wt% of a metallic Ti powder of 1.6 μm in average particle size and 20 wt% of a Co powder of 1 μm in average particle size. The resulting mixture was kneaded in a pressurized kneader at 160°C for 4 hours. This kneaded mixture was crushed to a size of 10 mesh or less to prepare the raw material of conductive magnetic ceramics B. In the next place, said raw material of ceramics A and said raw material of ceramics B were filled in turn in molds to shape pieces having structures shown in Figs. 3 - 6. After removal of the binder from the pieces, they were sintered in a nitrogen atmosphere, yielding ceramic composites. The dimensional change in of shaped pieces in sintering stage was as low as 0.3% and no crack developed in the pieces. Ceramics A and B exhibited resistivities of 10 Ωcm and 7×10^{-5} Ωcm, respectively, and magnetic flux densities of 1000 gauss and 200 gauss, respectively. In these sintered articles, the conductor and the insulator were strongly connected together through the reaction products Si_3N_4 and TiN. Articles shown in Figs. 3 and 4 are hollow cylinders and those shown in Figs. 5 and 6 are solid cylinders. The solid cylinder shown in Fig. 5 is a composite constructed of a central cylinder 5 of ceramic B and another cylinder 4 of ceramic A surrounding the former.

In similar ways of single-body shaping and single-body sintering, various ceramic articles in a laminate form having gradient functions or stepwise-changing functions can be produced by varying the kinds and proportions of powdery metal and powdery functional inorganic compound. Single-body sintered articles having substantially-continôus changes in function can be produced by reducing the thickness of component layers and increasing the number of such layers.

All the above obtained ceramic composites were found to contain about 5 vol% whiskers each of silicon nitride and titanium nitride.

Example 6

4 Parts by weight each of organic binders: a polyethylene wax, other synthetic wax, and stearic acid, for shaping purposes was added to 100 parts by weight of a mixture composed of 40 wt% of a metallic Ti powder of 1 µm in average particle size and 60 wt% of a $BaTiO_3$ powder of 1 µm in average particle size. The resulting mixtures were kneaded each in a pressurized kneader at 160 °C for 5 hours. These kneaded mixtures were crushed to prepare test materials. Disks of 50 mm in diameter and 20 mm in thickness were shaped from these test materials by using a mechanical press at a pressure of 1000 kgf/cm^2 and a temperature of 160 °C. These shaped disks were found to have packed particle volume fractions of at least 60%. The shaped disks were heated up to 500 °C at a heating rate of 3 °C/hr in an argon atmosphere to remove the binder, and further heated stepwise from 600 °C to 1300 °C for a long time in a nitrogen atmosphere, yielding sintered articles. Properties of these sintered articles are shown in Table 3. Therefrom it can be seen that capacitors having low resistivity and high permittivity were obtained according to the process of this invention with low dimensional change of shaped disks in sintering stage. These shaped disks (green bodies) can also be laminated one with another and sintered. A dielectric ceramic article having a magnetic property was obtained by combining the same dielectric particles as used above with magnetic particles. Similarly, a dielectric article having a catalytic property was obtained by combining the same dielectric particles with catalytic particles. Furthermore, dielectric articles having electron emission and heat conductivity were obtained.

Table 3

Dimensional change in sintering stage (%)	Dielectric constant	Resistivity (Ωm)
0.3	1500	7×10^{-7}

Example 7

7 Parts by weight each of organic binders: a polyethylene wax, other synthetic wax, and stearic acid, for shaping purposes was added to 100 parts by weight of a mixture composed of 30 wt% of a metallic Cr powder of 1 µm in average particle size and 70 wt% of a $PbTiO_3$ powder of 1 µm in average particle size. The resulting mixtures were kneaded each in a pressurized kneader at 160 °C for 5 hours. These kneaded mixtures were crushed to prepare test materials. Pieces (30 mm x 30 mm x 50 mm) were shaped from these test materials by using an extruder. These shaped pieces were found to have packed-particle volume fractions of at least 60%. The shaped pieces were heated up to 500 °C at a heating rate of 3 °C/hr in an argon atmosphere to remove the binder, and further heated stepwise from 400 °C to 1300 °C for a long time in a nitrogen atmosphere, yielding sintered articles. Properties of these sintered articles are shown in Table 4. Therefrom it can be seen that piezoelectric articles having low resistivity were obtained according to the process of this invention with low dimensional change of shaped pieces in sintering stage. Such ceramic articles can be used for parts, such as those of piezoelectric buzzers, gas lighters, and ultrasonic oscillators, which need to have high electroconductivity. Thus, the present ceramic articles will find expanded applications. Piezoelectric ceramics having a variety of functions can be obtained by combining the same piezoelectric particles as used above with differently functioning particles: magnetic particles, catalyst particles, thermal conductor particles, and electron emissive particles.

Table 4

Dimensional change in sintering stage (%)	Electromechanical coupling coefficient (%)	Resistivity (Ωm)
0.2	25	9×10^{-6}

Example 8

According to the procedure of Example 7, sintered articles having catalytic activity were prepared from a mixture of 40 wt% of a metallic Ti powder of 1 µm in average particle size with 60 wt% of a TiO_2 powder of 1 µm in average particle size by shaping and sintering. The dimensional change of shaped pieces in sintering stage was as low as 0.3%. The porosity and resistivity of the obtained articles were as low as 30 vol% and 2×10^{-5} Ωcm, respectively. It has proved that these articles having considerable electrical conductivity can be used as catalysts under heating and hence their catalytic efficiency can be made higher by a factor of 1.4 than that of catalysts consisting of TiO_2 alone. Powders of inorganic compounds other than TiO_2, when combined with suitable metal powders and sintered, also exhibit high catalytic efficiencies as compared with single-component catalysts. Sintered ceramic catalysts having a variety of functions were obtained by combining with the same particles as used above with differently functioning particles: magnetic particles, piezoelectric particles, thermal conductor particles, and electron emissive particles.

Example 9

According to the procedure of Example 6, sintered articles having electron emissivity were prepared from a mixture of 30 wt% of a metallic Si powder of 1 µm in average particle size and with 70 wt% of an LaB_6 powder of 1 µm in average particle size by shaping and sintering. The dimensional change of shaped pieces in sintering stage was as low as 0.1%. The porosity of the obtained articles was as low as 30 vol% while the resistivity thereof was 9×10^{-1} Ωcm. It has proved that these articles can be used at high temperatures with high current densities and hence the electron emissivity of these articles can be made higher by a factor of 1.3 than that of electron emitters consisting of LaB_6 alone. Powders of electron emissive compounds other than LaB_6, when combined with suitable metal powders and sintered, also exhibit high electron emission efficiencies as compared with single-component electron emitters. Electron emissive ceramic articles having various functions were obtained by combining the same LaB_6 particles as used above with differently functioning particles: magnetic particles, piezoelectric particles, and thermal conductor particles.

Example 10

A mixture of 70 wt% of a metallic Si powder of 1 µm in average particle size with 30 wt% of a CBN powder of 1 µm in average particle size was shaped by the doctor blade method to give multi-layer circuit boards. These shaped boards, provided with patterns of wiring, were laminated one with another and then heated from 500°C to 1350°C in an oxidizing atmosphere, yielding sintered boards. The dimensional change of shaped boards in sintering stage was as low as 0.1%. The obtained boards, useful for mounting, were found to a porosity as low as 20 vol%, a resistivity of 7×10^4 Ωm, and a thermal conductivity of 5 cal/cm•sec•°C. Boards for mounting provided with various functions are obtainable by combining such thermal conductor particles as used above with differently functioning particles: magnetic particles, piezoelectric particles, and electron emissive particles. In this way, applications of the present ceramic articles can be expanded to a large extent.

Example 11

Sintered articles were prepared from a mixture of 70 wt% of a metallic Al powder of 1 µm in average particle size with 30 wt% of an apatite powder of 1 µm in average particle size by shaping similarly to Example 7 using an extruder, followed by heating the shaped pieces from 500°C to 1350°C in an oxiding atmosphere. The dimensional change of shaped pieces in sintering stage was as low as 0.2%. The obtained articles are alumina-apatite compound materials useful as artificial bones. The porosity of these articles was as low as 0.2%. Thus, artificial bones complicate in shape could be formed in a simple manner.

Example 12

Sintered articles were prepared from a mixture of 70wt% of a metallic Ti powder of 1 µm in average

particle size with 30 wt% of an apatite powder of 3 µm in average particle size by shaping similarly to Example 7 using an extruder, followed by heating the shaped pieces from 500 °C to 1350 °C in a nitriding atmosphere. The obtained articles are TiN-apatite compound materials useful as artificial teeth. The porosity and resistivity of these sintered articles were as low as 15 vol% and 4 x 10^{-5} Ωm, respectively. The dimensional change of shaped pieces in sintering stage was as low as 0.3%. Because of having electrical conductivity, these artificial teeth can be processed by electric discharge. These artificial teeth can also be used as such without processing because of the low dimensional change of shaped pieces in sintering stage.

Example 13

According to the procedure of Example 6, sintered articles were prepared from a mixture of 40 wt% of a metallic Ti powder of 1 µm in average particle size with 60 wt% of a CoO powder of 1 µm in average particle size, by shaping and sintering. The dimensional change of shaped pieces in sintering stage was as low as 0.3%. The obtained articles, useful as sensors, were found to have a porosity of 30 vol% and a low resistivity of 2 x 10^{-5} Ωm. Because of having electrical conductivity these articles can be used as sensors under heating. This permits accurate measurements without being affected by humidity. Powders of compounds other than CoO, when combined with suitable metal powders and sintered, can also provide sensors which permit more accurate measurements than do single-component sensors.

Example 14

Similarly to Example 13, 30 wt% of a metallic Ti powder, 50 wt% of a CoO powder, and 20 wt% of a FeO powder, all the powders having an average particle size of 1 µm, were mixed together, then shaped, and sintered, yielding ceramic articles useful as temperature sensors. The dimensional change of shaped pieces in sintering stage was a low as 0.3%. The obtained sensors were found to a porosity of 30 vol%, a low resistivity of 5 x 10^{-5} Ωm, and a magnetic flux density of 200 gauss. Having electrical conductivity, these sensors can be used under heating, hence permitting accurate measurement without being affected by humidity. Moreover, these sensors have magnetic properties, hence being able to find new applications wherein these sensors are used not only as temperature sensors but also as magnetic sensors. Sensors having various functions were obtained by combining together sensor particles, piezoelectric particles, and catalyst particles other than magnetic particles.

Example 15

10 Parts by weight of an organic binder such as an ethylene wax, other synthetic wax, and stearic acid, for shaping purposes was added to 100 parts by weight each of mixtures of a metallic Cr powder of 1 µm in average particle size with a $PbTiO_3$ powder in different ratios. The resulting mixtures were kneaded each in a pressurized kneader at 160 °C for 5 hours. The kneaded mixtures were crushed to prepare test materials. Pieces in a plate form (30 mm x 30 mm x 2 mm) were shaped from these test materials, and finally, these plates different in blending ratio were laminated one with another so as to provide piezoelectric articles having gradient functions. These shaped structures were heated up to 500 °C at a heating rate of 3 °C/hr in an argon atmosphere to remove the binder, and further heated stepwise from 400 °C to 1300 °C for a long time in a nitrogen atmosphere, yielding sintered articles. The dimensional change of shaped structures in sintering stage was as low as 0.3%. These sintered articles are piezoelectric materials wherein resistivity and piezoelectric character change virtually continously in the direction perpendicular to the surface or interface of each component layer. Piezoelectric articles having various functions were also obtained by combining together magnetic particles, catalyst particles, thermal conductor particles, and electron emissive particles, instead of the piezoelectric particles.

Example 16

A binder was mixed with a raw material composed 50 wt% of a metallic Si powder of 1 µm in average particle size and 50 wt% of an Al_2O_3 powder of 1 µm in average particle size. Sheets were shaped from

the resulting mixture by the doctor blade method. Ti wiring patterns were formed on these shaped sheets, and these sheets were laminated one with another to give substates for mounting. These shaped laminates were heated up to 400°C at a heating rate of 3°C/hr in an argon atmosphere to remove the binder, and further heated stepwise from 500°C to 1350°C for a long time in a nitrogen atmosphere, yielding sintered laminates. The dimensional change of shaped laminates in sintering stage was as low as 0.3%. Each sintered laminate, useful as a substrate for mounting, was constructed of layers which were each composed of an Si_3N_4/Al_2O_3 substrate having a resistivity of 2 x 10^7 Ωm and a TiN wiring pattern having a resistivity of 4 x 10^{-7} Ωm which was formed on the Si_3N_4/Al_2O_3 substrate. A substrate having through-holes was also prepared by boring through-holes in one of the above shaped sheets, and sintering this sheet. Moreover, substrates for mounting having various functions were prepared by combining the above raw material powder with piezoelectric particles, magnetic particles, catalyst particles, thermal conductor particles, and electron emissive particles.

According to the present invention, it is possible to readily produce functional ceramic shaped articles by sintering shaped bodies with low dimensional change in sintering stage, the resistivity of the articles being variable from an insulator level to a conductor level, and the articles being provided with electrical and magnetic properties. Accordingly, the present ceramic articles can be used under special surrounding conditions for various applications without requiring additional processing such as cutting because of the low dimensional change in sintering stage, in other words, because the present ceramic articles are producible with high dimensional accuracy. Examples of the various applications of the present articles include capacitors, mechanical filters, acceleration sensors, piezoelectric elements of acoustic instruments and of telephones, temperature sensors, humidity sensors, dewing sensors, gas sensors, air pollution control catalysts, catalysts for petroleum refining, microwave filters, piezoelectric transformers, artificial bones, IC substrates, thermistors, electromagnets, magnetic cores of power transformers, magnetic shields, magnetic heads, electric leakage alarms, rotating machines of various sizes, motors, sensors, and electron beam condensers. Further, this invention contributes to the expansion of ceramic applications to such fields as aeronautic and space vehicles and related materials, steel industry, and ocean development.

Claims

1. A functional ceramic shaped article consisting of a reaction-sintered body which is composed of (i) particles (1) and/or fibers of at least one functional inorganic material having some of a piezoelectric function, dielectric character, magnetic character, heat conductive character, electron emissivity, catalytic activity, sensing function, and biological function and (ii) a ceramic (2) formed from metal particles during the sintering.

2. The article of Claim 1, wherein the ceramic (2) formed from metal particles during the sintering is at least one of oxides, nitrides, oxide-nitrides, and carbides of metals of groups III, IV, V, VI, and VIII of the periodic table.

3. The article of Claim 2, wherein the metal of said metal particles consists of at least one of Ti, Zr, V, Nb, Ta, Cr, Ce, Co, Mn, Nf, W, Mo, Al, Si, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Lu, and Th.

4. The article of Claim 1, wherein said particles (1) and/or fibers of at least one functional inorganic material are formed of at least one of PZT, $Pb(Zr, Ti)O_3$, $(Pb, Sr)(Zr, Ti)O_3$, $PbZrO_3$, $(Pb, Ba)(Zr, Ti)O_3$, $PbTiO_3$, $(Na, K)NbO_3$, $PbNb_2O_6$, $K_2O-PbO-SiO_2$, TiO_2, $2MgO-TiO_2$, $CaTiO_3$, $BaTiO_3$, $SrTiO_3$, $BaSnO_3$, $BaZrO_3$, SiO_2, PLZT, W, Th-W, LaB_6, $(Ba, Sr, Ca)O$, Zr-W, TiC, TaC, MgO, $SbCs_3$, Ag-O-Cs, BeO, Al_2O_3, $CaSO_4$, Fe, Co, Ni, Gd, Dy, Cu_2MnAl, Cu_2MnIn, MnB, Fe_3C, Mn_4N, MnBi, MnSb, MnAs, CrFe, CrO_2, EuS, EuO, CoPt, Fe_3Al, $MnFe_2O_4$, $FeFe_2O_4$, $SmFeO_3$, $CoFe_2O_4$, $NiFe_2O_4$, MnBi, $CuFe_2O_4$, $Li_{0.5}Fe_{2.5}O_4$, $MgFe_2O_4$, $Y_3Fe_5O_{12}$, $Gd_3Fe_5O_{12}$, Fe_3O_4, Fe_2O_3, $BaFe_{12}O_{19}$, $La_{0.5}Ca_{0.5}MnO_3$, CBN, SiC, $PtSiO_2$, $CaPO_4$, SnO_2, $ZnO-Bi_2O_3$, Y_2O_2S, ZrO_2, BeO, NiO, FeO, MnO, VO_2, V_2O_3, $LiNbO_3$, $LiTaO_3$, $LaF_3(Yb, Er)$, ZnS(Cu, Al), $Y_2O_3S(Eu)$, Pt, CaF_2, SnO_2, In_2O_3, ZnO, WO_3, NiO, CoO, Cr_2O_3, TiO_2, $LaNiO_3$, $(La, Sr)CoO_3$, $(Ba, Ln)-TiO_3$, CoO-MgO, AgX, Ag_2S, and PbO.

5. The article of Claim 1, in which electrical properties, magnetic properties or thermal properties are changed continuously or stepwise by changing continuously or stepwise the distribution density, configuration, or orientation of said functional inorganic particles (1) or fibers in the shaped body to be sintered.

6. A process for producing functional ceramic shaped articles, which comprises shaping a body from a mixture of particles (1) and/or fibers of at least one functional inorganic material selected from piezoelectric materials, dielectric material, highly heat conductive materials, catalytically active materials, electron

emissive materials, sensor materials, and biological materials with particles of at least one metal of groups III, IV, V, VI, and VIII of the periodic table, and reaction-sintering the shaped body in an atmosphere of reactive gas to form a ceramic (2) from the metal.

7. The process of Claim 6, wherein the reactive gas is a nitrogen-containing gas which react with particles of the metal to form its nitride.

8. The process of Claim 6, wherein said metal consists of at least one of Ti, Zr, V, Nb, Ta, Cr, Ce, Co, Mn, Hf, W, Mo, Al, Si, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Lu, and Th.

9. The process for Claim 6, wherein said particles (1) and/or fibers of at least one functional inorganic material are formed of at least one of PZT $Pb(Zr, Ti)O_3$, $(Pb, Sr) (Zr, Ti)O_3$, $PbZrO_3$, $(Pb, Ba) (Zr, Ti)O_3$, $PbTiO_3$, $(Na, K)NbO_3$, $PbNb_2O_6$, K_2O-PbO-SiO_2, TiO_2, $2MgO$-TiO_2, $CaTiO_3$, $BaTiO_3$, $SrTiO_3$, $BaSnO_3$, $BaZrO_3$, SiO_2, PLZT, W, Th-W, LaB_6, (Ba, Sr, Ca)O, Zr-W, TiC, TaC, MgO, $SbCs_3$, Ag-O-Cs, BeO, Al_2O_3, $CaSO_4$, Fe, Co, Ni, Gd, Dy, Cu_2MnAl, Cu_2MnIn, MnB, Fe_3C, Mn_4N, MnBi, MnSb, MnAs, CrFe, CrO_2, EuS, EuO, CoPt, Fe_3Al, $MnFe_2O_4$, $FeFe_2O_4$, $SmFeO_3$, $CoFe_2O_4$, $NiFe_2O_4$, MnBi, $CuFe_2O_4$, $Li_{0.5}Fe_{2.5}O_4$, $MgFe_2O_4$, $Y_3Fe_5O_{12}$, $Gd_3Fe_5O_{12}$, Fe_3O_4, Fe_2O_3, $BaFe_{12}O_{19}$, $La_{0.5}Ca_{0.5}MnO_3$, CBN, SiC, $PtSiO_2$, $CaPO_4$, SnO_2, ZnO-Bi_2O_3, Y_2O_2S, ZrO_2, BeO, NiO, FeO, MnO, VO_2, V_2O_3, $LiNbO_3$, $LiTaO_3$, LaFe(Yb, Er), ZnS(Cu, Al), $Y_2O_2S(Eu)$, Pt, CaF_2, SnO_2, In_2O_3, ZnO, WO_3, NiO, CoO, Cr_2O_3, TiO_2, $LaNiO_3$, $(La, Sr)CoO_3$, (Ba, Ln)-TiO_3, CoO-MgO, AgX, Ag_2S, and PbO.

10. The process of Claim 6, wherein the distribution density, configuration, or orientation of particles (1) and/or fibers of at least one functional inorganic material is changed continously or stepwise to shape a body, which is then heated in a nitriding atmosphere.

11. A low-resistivity and high-permittivity capacitor material consisting of a reaction-sintered body (2) which comprises both $BaTiO_3$ and Ti-nitride.

12. A low-resistivity piezoelectric material consisting of a reaction-sintered body (2) which comprises both $PbTiO_3$ and Cr-nitride.

13. A low-resistivity catalyst consisting of a reaction sintered body (2) which comprises both TiO_2 and the product of Ti reaction sintering.

14. A low-resistivity, electron emissive material consisting of a reaction-sintered body (2) which comprises both LaB_6 and the product of Si reaction sintering.

15. A multi-layer circuit board for mounting produced by forming reaction-sintered bodies (2) comprising both CBN and Si-oxide resulting from burning and having a pattern of wiring provided thereon, and laminating the bodies and sintering.

16. An artificial bone consisting of a reaction-sintered body (2) which comprises both apatite and Al-oxide resulting from burning.

17. An artificial tooth consisting of a reaction-sintered body (2) which comprises both apatite and Ti-nitride resulting from burning.

18. A temperature sensor consisting of a reaction-sintered body (2) which comprises both CoO and the product of Ti reaction sintering.

19. A temperature sensor consisting of a reaction-sintered body which comprises both FeO and Ti-nitride resulting from burning.

20. A piezoelectric material in which resistivity and piezoelectric character change continuously or stepwise from place to place.

21. A multi-layer circuit board for mounting which comprises (i) a reaction-sintered body comprising both Al_2O_3 and Si-nitride resulting from burning and (ii) a pattern of wiring formed on the reaction-sintered body.

FIG. 1

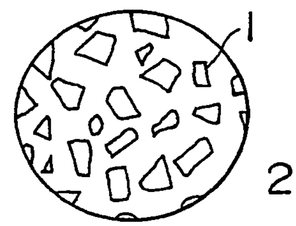


FIG. 2

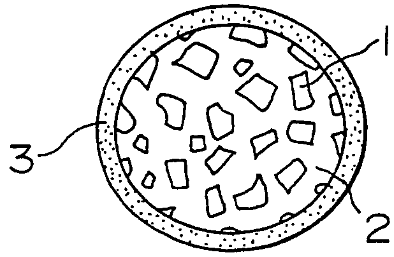


FIG. 3

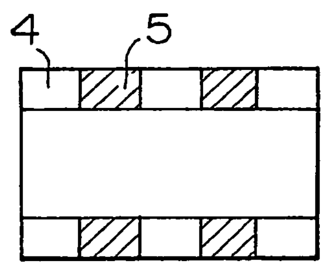


FIG. 4

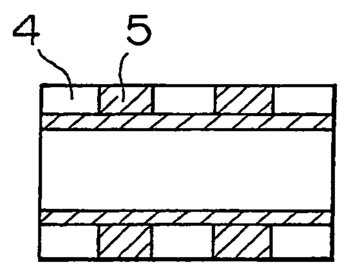


FIG. 5

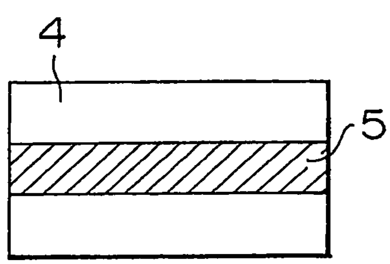
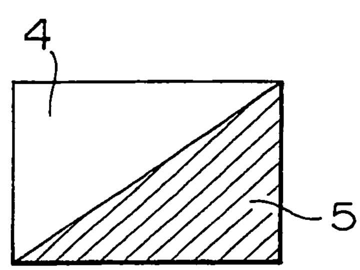


FIG. 6



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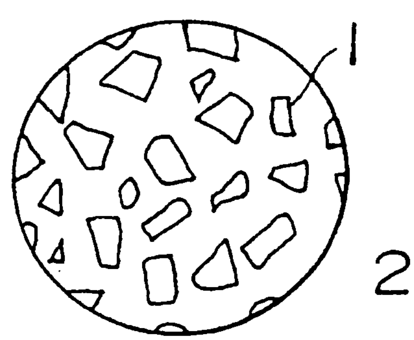
(54) **Functional ceramic shaped article and process for producing the same.**

(57) Functional ceramic shaped articles resistant to oxidation and corrosion can be produced with high dimensional accuracy by mixing (i) particles (1) and/or fibers of at least one functional inorganic material selected from piezoelectric materials such as $PbTiO_3$ and $PbZrO_3$, dielectric materials such as TiO_2 and $MgTiO_3$, magnetic materials such as Fe, Co, and Ni, heat conductive materials such as diamond and CBN, catalytically active materials such as γ-Al_2O_3 and zeolites, electron emissive materials such as W and Th-W, sensor materials such as NiO and FeO, and biological materials such as Al_2O_3 and apatite with (ii) particles of at least one of metals of groups III, IV, V, VI, and VIII of the periodic table, followed by shaping and reaction-sintering those mixtures.

FIG. 1



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Application Number

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	13-03-1991	KESTEN W.G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
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A	DATABASE WPIL/DERWENT abstract no. 87-316397 (45), 1987, Derwent Publications Ltd., London, GB; & JP - A - 62223065 (HITACHI) 01.10.1987 (cat. D) ---		
A	DATABASE WPIL/DERWENT abstract no. 88-004821 (01), 1988, Derwent Publications Ltd., London, GB; & JP - A - 62270481 (HITACHI) 24.11.1987 (cat. D) ---		
A	CERAMIC ENGINEERING AND SCIENCE PROCEEDINGS vol. 8, nos. 7,8, July-August 1987, pages 879-885, Westerville, OH, US; M.S. NEWKIRK et al.: "Preparation of Lanxide Ceramic Matrix Composites: Matrix Formation by the Directed Oxidation of Molten Metals" ---		TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	US-A-4 725 456 (T. WATANABE et al.) -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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